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The Annealing of Liquid Nitrogen Temperature Plastic Deformation and Radiation Damage in Lead*

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Abstract

Lead samples of several purities have been damaged at liquid nitrogen temperature. Two different damaging processes have been employed: compressive strain and irradiation by gamma rays from a Co^{60} source. Two studies of the effect of compressive strain have been performed: a study of the stored energy release during isochronal anneals from --170°C to +40°C and a study of the change in strain rate while under a constant stress during anneals from

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-180°C to +30°C. One study of the effect of radiation damage has been performed: a study of the change in attenuation of 10 Mc/sec ultrasonic pulses during anneals from -196°C to +20°C.

For the compressive strain studies, the purity of the samples has been varied over the range 99.9999% to 99% by the addition of thallium. It was found that purity has no effect on the ratio of energy stored to energy expended for the same amount of energy expended per gram atomic weight of lead. Increases in the impurity level cause increases in the amount of energy released during recovery. The results from the ultrasonic attenuation technique are interpreted using the Granato-Lücke theory of attenuation by dislocations and a model of defect migration to dislocations. Correlating the effect of impurities on recovery in the compressive strain studies with the results from the radiation damage study and the literature on copper, a tentative identification is made of the type of point defects migrating and the temperature range in which they migrate. In the temperature range -140°C to -110°C interstitial defects are released from impurity traps with activation energy (0.155 ± 0.010) eV and are then free to migrate. In the temperature region -90°C to -40°C free vacancies migrate with activation energy (0.31 ± 0.04) eV. Based on a vacancy mechanism for self-diffusion, the energy of formation of a vacancy is found to be 0.74 ± 0.05 eV.

I. INTRODUCTION

The low temperature physics group at Rensselaer Polytechnic Institute has been engaged for the last several years in the study of the phenomenon of superconductivity in lead, including the effects of plastic deformation[1]. Little is known about the properties of defects in deformed lead. The only low temperature studies known to the authors are those of Schenck[1] and Boesono[2], which are resistance recovery studies, and Khotkevich[3], which is of stored energy release. It was felt that a study in depth of the annealing of damaged lead would be of value in clarifying not only the properties of defects in lead but also the results of the superconductivity experiments.

We report here on the results of studying three properties during the annealing of damaged lead crystals: the release of energy stored by plastic deformation (stored energy of cold work), strain under constant stress following an initial strain (creep), and ultrasonic attenuation changes after gamma irradiation (radiation damage). The organization of this paper is fairly standard with the possible exception that discussion relating specifically to the results of a single technique has been included as a sub-section of the corresponding section in part III, Analysis and Results. Part IV is reserved for the discussion in which results of the several techniques must be considered together.

II. EXPERIMENTAL TECHNIQUES

Stored Energy Experiment

Specimen Preparation

Three different purities of lead were investigated: 99.9999%, 99.9% and 99%. The 99.9% and 99% pure lead samples were prepared by doping

99.999% pure lead with thallium of similar purity. All materials were supplied by the United Mineral and Chemical Corporation. The samples were cast in vacuum of 10^{-6} torr in the form of 3/8 inch diameter rods approximately 5 inches in length and were initially single crystal. After casting, the rods were cut into 3/4 inch lengths and a 1/16 inch diameter hole was drilled through the center of each specimen perpendicular to the 3/4 inch length. Two 3/16 inch deep, 1/16 inch diameter holes were drilled in each of the specimens for future thermocouple and hanging wire insertion. The specimens were then etched, weighed, and their dimensions recorded. Into the hole through the specimen Evanohm wire wound heaters of approximately 300 ohms were emplaced using epoxy cement.

Cold Working of the Specimens

Figure 1 illustrates the apparatus used. All electric wiring has been omitted from the figure. A pumping line (not shown) led from the specimen chamber by means of which the specimen chamber was kept below 8×10^{-6} torrs during the experiment. The specimen chamber was vacuum sealed by means of the lead gasket which was pressed between the bottom plate and the flange, both of which had sharp edges for better vacuum sealing, as illustrated by Scott[4]. This arrangement worked well and each gasket could be used a number of times.

Before deformation the test specimen was located at the bottom of the specimen chamber directly below the straining tube. The system was then evacuated. A frame was placed around the specimen chamber and was under tension during the compression of the test specimen. The frame and not the solder joints of the cryostat was thus stressed. The

specimen chamber was cooled to liquid nitrogen temperature and the lower part of the straining tube was filled with liquid nitrogen. The threaded handle in the frame was then used to bear against the calibrated spring which rested on the straining tube which in turn transmitted the stress to the test specimen at the bottom of the specimen chamber. The tube slid through the O-ring seal. The load-compression curves were obtained by means of the three dial gauges. The energy expended in compressing the test specimen was obtained by integration of the load-compression curve. After the test specimen was strained, the straining tube was raised. By means of the hanging wire connecting it to the test specimen, the test specimen was raised from the bottom of the specimen chamber to a symmetrical position with respect to the standard specimen. The specimens were left undisturbed in this position during the course of the subsequent anneals. This eliminated the problem of the change in thermal contacts caused by moving the specimens.

The Technique of the Stored Energy Experiment

The method used in this experiment was that of isochronal annealing in which the temperature was raised at a predetermined rate with null temperature difference maintained between the standard and test specimens. A similar technique has been used by Clarebrough[5], et al. After straining, three consecutive anneals were performed at a controlled rate of warmup between 2° and 5°C per minute. During the first anneal the cold worked specimen released its stored energy and less power was required to heat the test specimen at the predetermined rate than in subsequent anneals. Integrating the power difference between the first and subsequent anneals, ΔP, over the time of the anneal, the total energy stored

was obtained. It should be kept in mind that null temperature difference (± 0.10°C) was maintained between the specimen chamber and the specimens to ensure that no heat was conducted to or from the specimens which would affect the stored energy determinations.

Electrical Wiring

Thermocouple arrangement. Three thermocouples were used. All were made from No. 36B and S gauge chromel-constantan wire supplied by Thermo-Electric Company. One thermocouple, which measured the temperature of the system led to the standard specimen. Readings of the temperature were marked on the record during the isochronal anneals; other temperatures were readily interpolated. A differential thermocouple led from the standard specimen to the test specimen. A second differential thermocouple led from the standard specimen to the specimen chamber wall. A block diagram of the arrangement is presented in Fig. 2.

The specimen-specimen differential thermocouple was connected to a reversing switch and then to a Keithley Milli-Microvolt Amplifier (#149). The temperature difference, together with the test specimen power input, was monitored on the two pen recorder. The temperature difference signal was reversed often during the anneals to eliminate the effect of contact potentials. Null temperature difference was taken to be the average of the reversed signals as seen on the recorder.

Heater circuits. The specimen chamber heaters were mounted externally on the specimen chamber and controlled manually. By judicious use of the variable resistor in the circuit, the temperature difference between the specimen chamber and the standard specimen was held to less than ± 0.10°C during the isochronal anneals. The specimen chamber was

heavy walled copper to insure temperature uniformity.

The specimen heaters were connected to a foot long length of #40 copper wire which led into #20 copper wire which was wrapped and epoxy cemented to the thermal grounding posts. From the specimen chamber the wires led into a circuit which is illustrated in Fig. 2. The emf leads from the test specimen heater ran into a precision voltage divider to obtain a voltage reading in the range of the potentiometer. The small unbalance signal from the potentiometer was fed into the other input of the recorder, where full scale deflection was 1 millivolt.

The voltage to the standard specimen was left unchanged during the experiments, and the test specimen heater was controlled by the variable resistor in the circuit so that the apparent temperature difference between the two specimens was less than $\pm 10^{-3}$ °C. While the individual junctions are not reproducible enough to be sure that the actual temperature difference was this small, the temperature differences could be reproduced from one run to the next to this accuracy. It is this type of reproducibility which is crucial to the experiment. The current through the standard specimen was measured by reading the voltage drop across the ten ohm standard resistor. This voltage was measured every ten degrees during the anneals. Any corrections to the voltage measurements due to variations in the output from the power supply were based on this measurement. Corrections were of the order of 10% of the stored energy.

Creep Experiment

This part of the research used the same apparatus and specimens as the stored energy experiment. Using the strain apparatus the specimen was strained 10% at liquid nitrogen temperatures. With the load still

on the specimen the system was warmed at the rate of 3 to 4°C per minute. The change in length of the test specimen was obtained from the deflections of the dial gauges.

Radiation Damage

The radiation damage study was performed using ultrasonic apparatus and techniques which are essentially identical to those described by Love, et al[6], and will not be discussed further here. The transducer was a 10 megacycle x-cut quartz disc made by Valpey Corporation and was bonded to the specimen with Nonaq stopcock grease.

The one specimen used was approximately a cube one centimeter on an edge, cut from a 99.999% pure single crystal lead ingot obtained from Unimet Corporation. (See ref. 6 for semiquantitative analysis of another sample cut from this ingot.) The crystal was oriented so that the ultrasonic pulses traveled along the [110] direction. The specimen's (110) faces were hand lapped flat and parallel as required for the ultrasonic measurements.

The specimen chamber consisted of a simple frame in which the specimen rested during the irradiation and anneals. The specimen rested between two styrofoam forms in the frame. During the irradiation the frame and specimen were kept in a dewar of liquid nitrogen inside a brass water tight can. The can was necessary because the irradiation took place in a Co^{60} source which was located 15 feet under water. The temperature was controlled during the anneals by raising or lowering the frame above the liquid nitrogen level in the dewar. The temperature was measured by means of a chromel-constantan thermocouple which was attached to the specimen. The isothermal anneals were kept to within

± 0.10°C using this system. Anisothermal anneals were performed typically at the rate of 3-4°C per minute.

III. ANALYSIS AND RESULTS

The results of the three experimental techniques used in this research will be presented in this part. Only those conclusions which can be made without correlation with the other results will be described here, the remainder being deferred until Part IV.

Stored Energy of Cold Work

The results of the first 26°C above liquid nitrogen temperature are not reported because it required approximately that range of temperature to attain null temperature difference between the specimens and the specimen chamber. The voltage drop, V, across the heater in the test specimen was monitored continuously during the anneals. Since the voltage drop across the heater was of the order of five volts and the voltage difference between the first anneal after strain and subsequent anneals was twelve millivolts at maximum, the power difference between the anneals can be approximated by the expression

$$\Delta P = 2V\Delta V/R - V^2\Delta R/R^2 \qquad (1)$$

Here R is the resistance of the test specimen heater, and ΔV and ΔR refer to differences between the first and subsequent anneals. The last term of Eq. 1 was ignored in all calculations since it was always less than 0.1% of the first term. In order to obtain the stored energy, E_s, Eq. 1 was integrated over the length of time of the anneal, t',

$$E_s = (2V/R) \int_0^{t'} \Delta V dt \qquad (2)$$

In practice, this integration was carried out from the data plots with the aid of a planimeter.

In order to verify that the observed changes in voltage were due to stored energy release and not some extraneous effect, various experimental checks were performed. A dummy run was performed where the procedure followed that of a typical stored energy determination except that the straining tube was just brought into contact with the test specimen and no stress was applied. The variation in voltage drop across the test specimen heater during three subsequent anneals led to a stored energy uncertainity of ± 6%.

In order to minimize the problem of adsorption of gases on the surfaces of the specimens, the specimens and specimen chamber were outgassed at an elevated temperature prior to the compression. Since the system was kept evacuated until the stored energy determination was completed little release of adsorbed gases during the anneals was expected. The absence of any spurious peaks in the dummy run established the fact that adsorption of gases was not a problem.

Another source of error was that due to the effect of straining the samples. It appears that, due to the initial compression, a worse thermal contact was created between the test specimen and its heater than existed prior to compression. In the first anneal after straining the thermal contact improved. Therefore, the temperature difference between heater and sample was greater and more heat flowed through the leads from the test specimen heater to the specimen chamber during the first anneal than in subsequent anneals. This led to lower values of stored energy than are correct. In fact, if the thermal resistance

between the specimen heater and the specimen chamber was low enough apparent negative stored energies were obtained.

This effect was investigated by measuring the temperature difference between the specimen surface and the heater winding during a series of anneals by means of an additional thermocouple. Variations of up to three degrees were found between the first anneal and subsequent anneals after straining. By increasing the thermal resistance between the specimen heater and the specimen chamber the error in stored energy due to this effect was kept to less than ± 6%.

This change in thermal contact effect may have caused errors in other stored energy studies. Welber and Webeler[7], using an apparatus similar to ours, studied copper after fatigue and found apparent negative stored energy release. It is possible that those results suffer from not taking into account this thermal contact effect.

The results of expending similar amounts of energy on different specimens led to similar stored energy curves with variations of up to 4% between a pair of typical runs. Considering this variation together with the uncertainities mentioned above the total error in the stored energy values is estimated to be ± 15%.

The stored energy release is markedly affected by different impurity levels in lead. Figure 3 illustrates typical stored energy release curves from three different purity samples all strained to similar amounts of energy expended. As seen, the increase of the impurity level increases the energy released at lower temperatures. The peak centered in the region near -20°C is associated with recrystallization. The smaller peak in the -80°C to -60°C region is associated with point defect

migration. The maximum release rate in the recrystallization stored energy peak rises from -20°C in 99.9999% pure lead to -12°C in the 99.9% pure lead to -5°C in the 99% pure lead.

The ratios of the total amount of energy stored to the energy expended in compression obtained from a series of experiments on samples of different purities are presented in Fig. 4. The results indicate that the impurity level does not affect the energy stored for the same amount of energy expended per gram. As Fig. 3 indicates, however, impurity does change the fraction of the energy released in the various temperature ranges.

Khotkevich, et al have studied the stored energy release in plastically deformed lead.[3] They crushed 0.2 mm diameter, 50 mm lengths of lead (purity unstated) in a press at liquid nitrogen temperature. Their results indicate a general agreement as to the high percentage of energy stored at low expenditures. At higher expenditures their results indicate considerably higher storage. It may be that experimental differences are sufficient to explain this discrepancy.

Discussion. The small peak near -70°C will be associated with vacancy motion in part IV. Attempts to analyze the shape of this peak by the method of Nicholas[8] or to observe a shift as a function of rate of change of temperature were unsuccessful. The large peak, associated with recrystallization, is seen to move to higher temperatures as the impurity level is raised. This is a result of impeded grain boundary and dislocation motion in the impure material. Such effects have been studied in detail by Aust and Rutter.[9]

The large percentage of energy stored when small amounts of energy are expended is not in agreement with studies of other face centered cubic metals[10]. It implies that for small strains there are few defects formed which are not stable and sedentary at liquid nitrogen temperature.

The increase of the fraction of the total energy released during recovery as impurities are added may be explained as follows: Point defects are thought to be formed during deformation primarily in lines behind moving jogs in dislocation lines. As such the tendency to cluster will be considerable and will be maximum in the pure material, where trapping centers are rare. Thus, in the pure material, most of the point defects will have clustered and not release further energy until recrystallization has commenced. In the impure material the point defects will be trapped as singles or small groups and may move at lower temperatures. Their motion may also allow considerable dislocation climb and rearrangement.

The decrease in the percentage of energy stored with increasing expenditure is a normal result, explained by the fact that when a large amount of energy is spent there are more dislocation intersections and more point defects produced as well as an increase in the dislocation density. There are then both more point defects with finite mobility at 77°K formed and also a larger probability of dislocation interaction and annihilation.

Creep

The results consist of the change in length of the specimen undergoing a constant compressive stress after an initial ten percent strain,

while the temperature is raised at the rate of 3-4°C per minute. In order to expose the regions of temperature where the strain rate changes, graphs of the change in strain, $\Delta\ell/\ell$, during the previous ten degrees, were plotted versus temperature. Two different purity lead samples were investigated: 99.9999% pure lead and 99% lead -1% thallium. The data from the 99% lead are presented in Fig. 5. These results exhibit little increase in the strain rate until -130°C is reached where a small peak occurs. Little additional structure is observed until -70°C. The results from 99.9999% pure lead lacked the -130°C peak but showed the higher temperature rise beginning about -80°C.

Discussion. The difference in behaviour near -130°C of the samples of different purity again suggests a release of point defects from impurity traps. The released defects must be ones which can aid dislocation climb thereby giving rise to the temporary softening when they reach the dislocations. The general rise at higher temperatures may initially be associated with other point defects migrating but is ultimately dominated by recrystallization.

Radiation Damage

Isochronal anneals. The technique used here to study the small amount of damage introduced by the gamma irradiation was ultrasonic attenuation. The picture is one of attenuation primarily due to the motion of dislocations in the ultrasonic stress field. When point defects migrate to the dislocations their motion is impeded and the attenuation is reduced. In the present experiment the third echo was monitored continuously on the recorder during all anneals while the initial pulse was held fixed. Figure 6 illustrates the results of such

monitoring during the following operations: (1) the pre-irradiation cooling from room temperature to liquid nitrogen temperature, (2) the post irradiation annealing up to +20°C, (3) and (4) a subsequent cool down-irradiation-warmup cycle (performed after the transducer bond was changed), and (5) an unirradiated warmup to +20°C.

In order to check that the irradiation effects observed were associated with the sample and not with the transducer and bond, a similar irradiation was performed with the same transducer and bonding agent on a commercial aluminum alloy sample. In such a sample, little effect is expected due to migration of point defects created by the irradiation because the impurities pin the dislocations in place throughout the process. No effect was found on the pulse height indicating that the effect seen in lead is associated with the damage done to the sample during the irradiation.

In Fig. 6 the regions of pulse height increase (corresponding to attenuation decrease) are thought to be associated with the arrival of point defects at the dislocations. For convenience, we will refer to the low temperature region -140°C to -115°C as stage III and -90°C to -40°C as stage IV. The similarity of these regions to the corresponding stages in copper will be discussed in section IV.

Isothermal anneals. To obtain activation energies of the migrating defects in stages III and IV the following model was developed. The model is based on the Granato-Lücke[11] theory and a publication by Shaw[12], et al. We assume that the gamma rays have created a uniform distribution of isolated defects in the single crystal and that the crystal possesses

a uniform dislocation density. The number of pinning points created at the dislocations is taken as directly proportional to the number of defects which disappear from the bulk of the crystal. The dislocations are represented as perfectly absorbing circular cylinders of finite small radius r_o and infinite length.

Following the method outlined by Dienes and Vineyard[13], the solution of the diffusion problem of point defects migrating to the dislocations is simplified by dividing the crystal into imaginary cylinders of radius r_1 such that each cylinder contains one dislocation at its center. Further, the surface of the cylinder at r_1 is considered perfectly reflecting and r_1^2 is taken equal to $1/N_o$ (N_o is the dislocation density).

The diffusion equation for the total number of defects per unit length of the cylinder, n(t), then reduces to

$$dn(t)/dt = -Kn(t) \tag{3}$$

where $K = 2\pi N_o D \ell n(r_1/r_o)$ and D is the diffusion coefficient. This then leads to Eq. (4)

$$\ell n[n(t)/n(0)] = - t(2\pi N_o D_o \ell n(r_1/r_o) \exp -Q/kT \tag{4}$$

The concentration of pinning points at the dislocation line, $c_D(t)$, is

$$c_D(t) = c_D(0) + R[n(0) - n(t)] \tag{5}$$

where $c_D(t)$ is the average linear density of pinning points at the start of the isothermal anneal. R is the proportionality constant relating the change in the number of defects in the cylinder to the number of pinning points created at the dislocation line.

We now assume that the total attenuation of the pulse is due to the dislocation vibrational loss. The linear concentration of pinning points at the dislocation line is inversely proportional to the average loop length, L, of the dislocation lines. At frequencies well below resonance Granato and Lücke[11] showed that the attenuation is given by the relation

$$\alpha = BL^4\omega^2 \tag{6}$$

where ω is the angular frequency of the pulses. B is a proportionality constant depending upon the velocity of sound in the material, the dislocation density, and other parameters. Therefore, for the present fixed frequency and dislocation density conditions

$$c_D(t) = A\ \alpha^{-1/4} \tag{7}$$

where A is a proportionality constant. Realizing that, for very long times, n for the diffusing species will go to zero, equations (5) and (7) can be combined to yield the ratio $n(t)/n(0)$.

$$\frac{n(t)}{n(0)} = \frac{\alpha^{-1/4}(\infty) - \alpha^{-1/4}(t)}{\alpha^{-1/4}(\infty) - \alpha^{-1/4}(0)} = f(\alpha) \tag{8}$$

Combining Eq. 8 with Eq. 4 we obtain

$$\ln f(\alpha) = - t/\tau \tag{9}$$

where $1/\tau = 2\pi N_o D_o \ln(r_1/r_o)\ \exp - Q/kT$

Experimental values of $\ln f(\alpha)$ plotted against time should then be linear with a slope of $-1/\tau$. When many values of τ and T have been obtained experimentally a plot of $\ln 1/\tau$ against $1/T$ should be linear with a slope of $-Q/k$.

In the above manner activation energies of the mobile defects have been obtained from isothermal anneals in the stage III and stage IV

temperature regions. From these data plots of ℓn f(α) versus time were made. These are illustrated in Figs. 7 and 8. The plots of ℓn 1/τ are shown in Figs. 9 and 10. The activation energies obtained from the slopes are: in stage III, 0.155 ± 0.010 eV, in stage IV, 0.31 ± 0.04 eV.

Discussion. In stage III the ℓnf(α) versus t plots show a marked tendency to become non-linear as time progresses. Some of this tendency may be attributed to errors in the value of α(∞) used. If the isothermal anneal is not allowed to continue for a sufficiently long time, the α(∞) value obtained may be smaller than the correct value. This does not affect f(α) values near the start of the anneal as much as it affects later values. Therefore, the initial slope of the ℓn f(α) versus time plots have been used in arriving at the activation energy for stage III.

Allowing a reasonable uncertainity in α(∞) does not seem to account for the size of the deviation of the ℓn f(α) curve from linearity and some other explanation must be sought. It would seem quite reasonable that this deviation is a result of a competing process whereby pinning points are annihilated. One such possible process would be a diffusion of the pinning points along the dislocations until they recombine with others, thus lowering the effective number. More research is needed to establish this picture, however.

In stage IV the ℓn f(α) versus time plots are linear indicating migration of defects to the dislocations to form stable pinning points. Following an isothermal anneal in stage IV the temperature can be raised to -40°C before further change in attenuation occurs. The decrease of the pulse height in the temperature region above -40°C is continuous as the temperature is further raised. This is attributed to the disappear-

ance of the pinning points which have been created by point defects, by the recrystallization mechanism. No isothermal studies have as yet been made of this recrystallization region. For convenience, the region from -40°C to +30°C will be referred to as stage V.

IV. DISCUSSION

Identification of the Migrating Defects

It is believed that essentially all of the defects created by the gamma irradiation of lead are simple Frenkel defects. In addition the concentration to be expected from the present irradiation is very small. Under these conditions the only recovery stages observed will be those associated with the migration of interstitials and vacancies and with recrystallization. However, the free defects can be trapped at impurities with the result that there will be a series of recovery stages depending on the different types and number of impurity traps. This interpretation has been presented by Hasiguti[14], Martin[15], Seeger[16], and Sosin[17] to explain stages II and III in copper. The impurity studies in the stored energy and creep experiments indicate a similar effect in lead. In direct analogy with the picture developed by these authors for copper we suggest that stage III in lead is associated with the release of interstitials from impurity traps, stage IV is the migration of free vacancies, and stage V is recrystallization.

Consistency of the Results with the Defect Identification

Stage III

According to the data on copper, stage III exhibits a second order nature during the resistivity recovery. Our radiation damage results

indicate that the stage III defect migration as observed by the attenuation technique in lead is essentially first order. There is no contradiction present if one realizes that in stage III the interstitials migrate to vacancies and dislocation sinks. The resistivity recovery is sensitive to annihilation at both types of sinks, while the attenuation technique is sensitive only to the defect migration to the dislocations. Because of the high levels of damage required for the resistivity experiments, recombination with the associated second order kinetics dominates. In the present attenuation experiment, the migration of the interstitials to the dislocations should dominate over recombination because the number of vacancy sites available for recombination is estimated to be at most 10^{-4} of the number of dislocation sites available. This is based on an estimate of the damage, calculated using the theory of Seitz and Koehler[18]. The threshold energy for displacing a lead atom, based on the damage estimate, is less than 21 eV.

Both the stored energy and creep experiments indicate an enhancement of annealing in the vicinity of stage III as impurities are added. This might be explained either by the impurity-trapped defect hypothesis or by considering that higher prestrain dislocation densities may have been present in the impure material yielding more point defects upon deformation. No dislocation density measurements have as yet been made in the present experiments but there appear to be two pieces of indirect evidence which speak against significant differences in dislocation density. First, the total energy stored upon deformation is independent of impurity level indicating that the deformation processes are similar in the pure and doped materials. Second, the stage IV stored energy peak

is not significantly increased as the impurity level is increased but rather fades into the general recovery background indicating again that the total number of point defects formed is perhaps not very different while impurity trapping will be.

That stage III involves interstitials rather than some other kind of defect must rest for the present upon the analogy of lead with copper and the calculations and experiments on copper which support this model. In addition it should be pointed out that the residual impurities in the radiation damaged specimen are probably not predominantly thallium while stage III occurs in the same temperature region for the thallium doped and the pure specimens used here. Thus the proposed model requires a very weak dependence of interstitial-impurity binding energy upon impurity species.

Boesono[2] has studied the resistivity recovery of lead which had been cold-rolled at liquid nitrogen temperature. He interpreted the recovery in the -130°C region as being due to vacancy migration and obtained an activation energy of migration of 0.48 ± 0.05 eV for that region. Because of the briefness of his paper and the absence of detail, it is impossible to fully understand the difference in results. We believe that the recovery taking place in the -130°C temperature region is associated with the present stage III and that his vacancy recovery is hidden in the recrystallization region. This takes place at a very low temperature in the Boesono study due to the large amount of strain applied to the specimens during the cold rolling (70%). Boesono's data show an enhancement of the recovery in the -130°C region with increasing impurity levels.

This is in agreement with our picture of interstitials being released from impurity traps in this stage. The resistivity recovery of tensily strained lead at liquid helium temperatures studied by Schenck[1] indicates faintly that there are separate stages III, IV, and V in approximate agreement with the stages seen in this research.

Stage IV

In the temperature range -90°C to -40°C both the stored energy and radiation damage experiments indicate an anneal taking place. The stored energy shows no increase in stage IV as impurity is added and, in fact, at the 1% thallium level, the peak has faded completely into the general recovery background. Neither the creep experiments illustrated in Fig. 5 nor those carried out on the high purity material show a stage IV peak which can be clearly separated from the onset of recrystallization. In view of the nature of those measurements this is not unreasonable.

The energy of self-diffusion in lead has been established by Nachtrieb[19] to be 1.05 ± 0.01 eV. It has been established in copper that the diffusion mechanism is that of vacancies by Kirkendall[20]. It is expected that the same is also true for lead. Then the sum of the energy of migration found in stage IV and the formation energy of a vacancy in lead should yield the Nachtrieb result. Thus the energy of formation of a vacancy in lead is found to be 0.74 ± 0.05 eV. This is consistent with the result of Van Duyn who found that this energy must be greater than 0.4 eV.[21]

Stage V

During the first anneal after irradiation, the pulse height in this stage decreases continuously to the pre-irradiation value. This is

associated with the thermal release of defects from dislocations, a process which is often thought to give rise to recrystallization and here allows release of pinning points from the dislocations. Both the creep and stored energy measurements are entirely consistent with recrystallization in this region around -20°C.

Summary and Conclusions

The results of the different techniques used in this study of lead have been put into a self-consistent form. A method of obtaining activation energies from isothermal anneal data using the ultrasonic attenuation technique after irradiation has been presented. The main assumptions made in arriving at the activation energies are based on the Granato-Lücke theory which has not been verified in lead at the frequencies used in this research. The principal justification for concluding that the analysis is correct is that the data fits very well into the activation energy analysis.

The identification of the migrating defects is tentative and is guided by the much more extensive work on copper. The most self-consistent identification is that of interstitials migrating from impurity traps in the -140°C to -110°C region, free vacancies migrating in the -90°C to -40°C region, and recrystallization occurring, for the strains and purities studied here, above -60°C. Based upon this identification the binding energy of interstitials to impurities is 0.155 ± 0.005 eV, the energy of migration of vacancies is 0.31 ± 0.04 eV, and, using Nachtrieb's self-diffusion data[19], the energy of formation of a vacancy is found to be 0.74 ± 0.05 eV. One might expect the interstitial

impurity binding energy to be strongly dependent upon the impurity type but, within the limitations of the present experiment, this does not seem to be the case.

A surprising result of this research is the large fraction of the expended energy which is stored upon small deformations at liquid nitrogen temperature. As much as 80% of the energy expended is stored in lead while in copper only 20% storage is observed for the same amount of energy expended per gram atomic weight[10]. This might result from different initial dislocation configurations in the two materials or be caused by a more fundamental difference.

Several questions remain from this research and are now being pursued. Foremost is the general applicability of the Granato-Lücke theory at the very literal level employed here. Of a more detailed nature the identification of the processes leading to the pulse height drops in Fig. 6 above stage III and IV requires further work. It does appear, however, that the ultrasonic technique can provide quantitative information concerning point defect annealing.

FIGURE CAPTIONS

Fig. 1 - Section diagram of the strain apparatus and specimen chamber used in the stored energy and creep studies.

Fig. 2 - Schematic diagram of the thermocouple and electrical arrangement in the stored energy and creep studies (the specimen chamber's external heater circuit is omitted).

Fig. 3 - The power difference between the later anneals and the first anneal after strain.

Fig. 4 - Percentage of energy stored versus energy expended for several purities of lead.

Fig. 5 - Three creep experiments performed on different 99% lead-1% thallium samples.

Fig. 6 - The change of pulse height of the third echo during temperature cycles. The two upper curves were taken following irradiation and the lower curves were unirradiated comparison runs.

Fig. 7 - $\ell n\ f(\alpha)$ versus time during typical stage III anneals.

Fig. 8 - $\ell n\ f(\alpha)$ versus time during typical stage IV anneals.

Fig. 9 - $\ell n\ 1/\tau$ versus 1/T based upon Fig. 7 and additional data, (stage III).

Fig. 10 - $\ell n\ 1/\tau$ versus 1/T based upon Fig. 8 and additional data, (stage IV).

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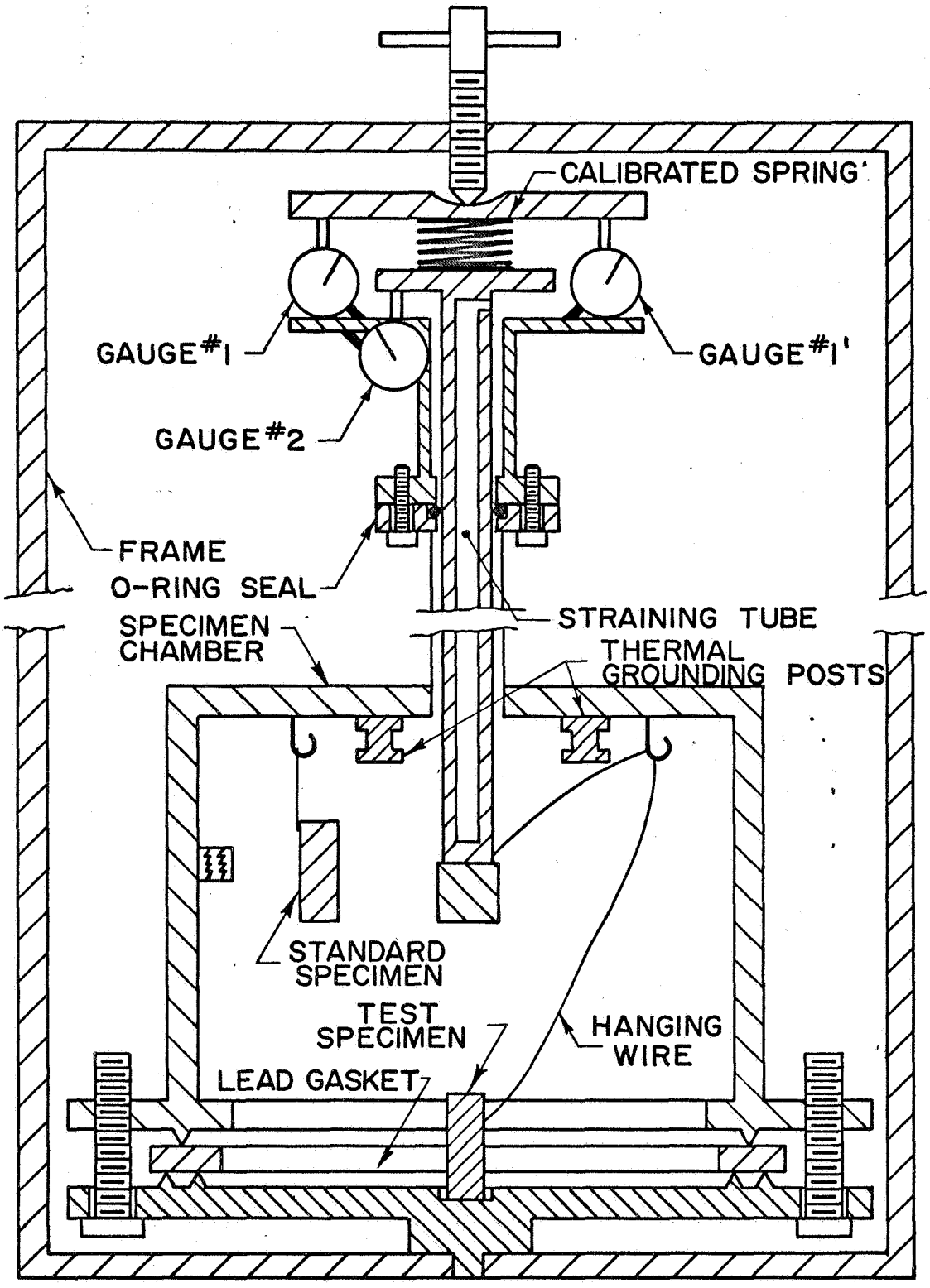
CALIBRATED SPRING
GAUGE #1
GAUGE #1'
GAUGE #2
FRAME
O-RING SEAL
SPECIMEN CHAMBER
STRAINING TUBE
THERMAL GROUNDING POSTS
STANDARD SPECIMEN
TEST SPECIMEN
HANGING WIRE
LEAD GASKET

Figure 1

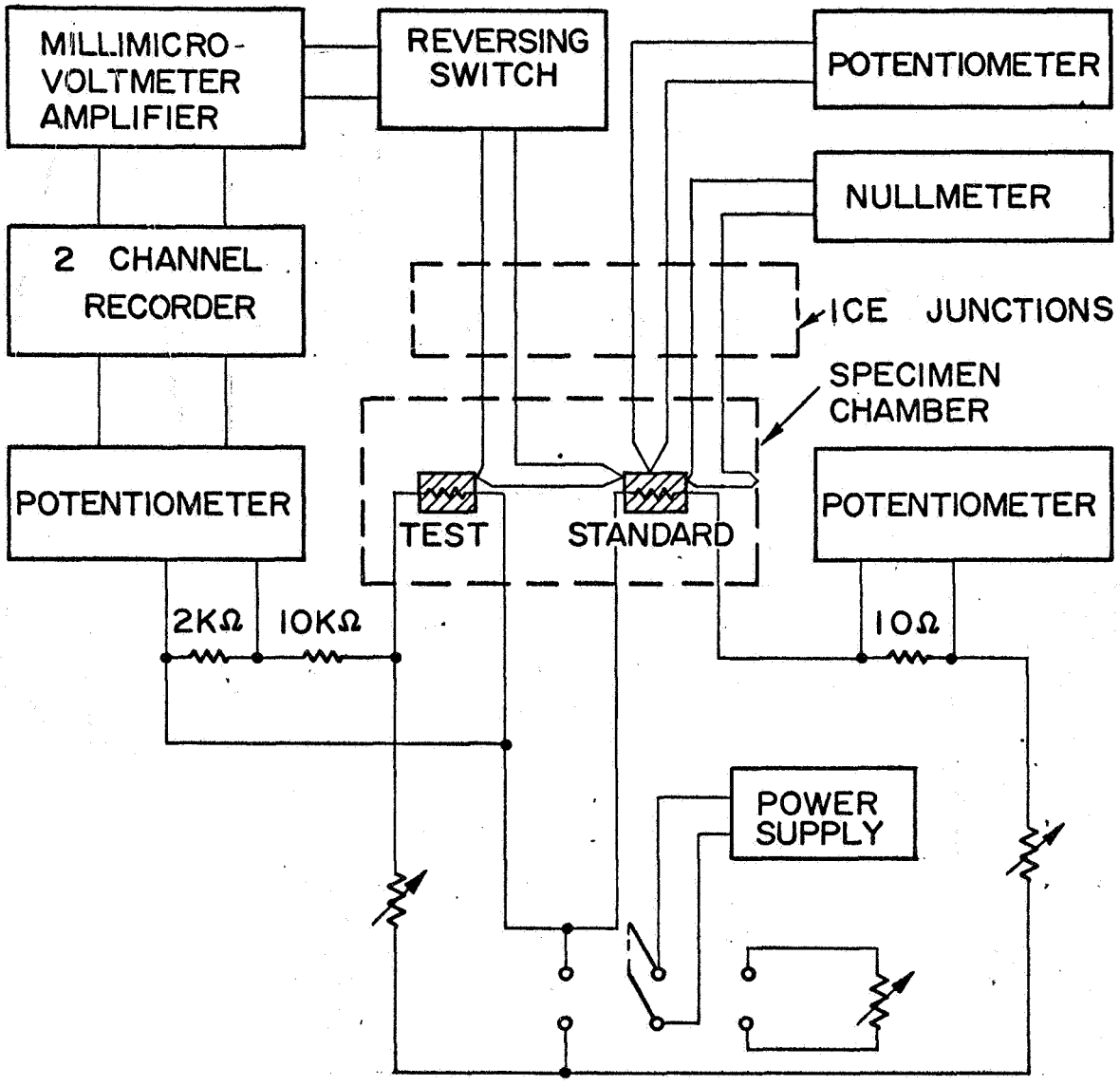
MILLIMICRO-
VOLTMETER
AMPLIFIER
REVERSING
SWITCH
POTENTIOMETER
NULLMETER
2 CHANNEL
RECORDER
ICE JUNCTIONS
SPECIMEN
CHAMBER
POTENTIOMETER
TEST
STANDARD
POTENTIOMETER
2KΩ
10KΩ
10Ω
POWER
SUPPLY

Figure 2

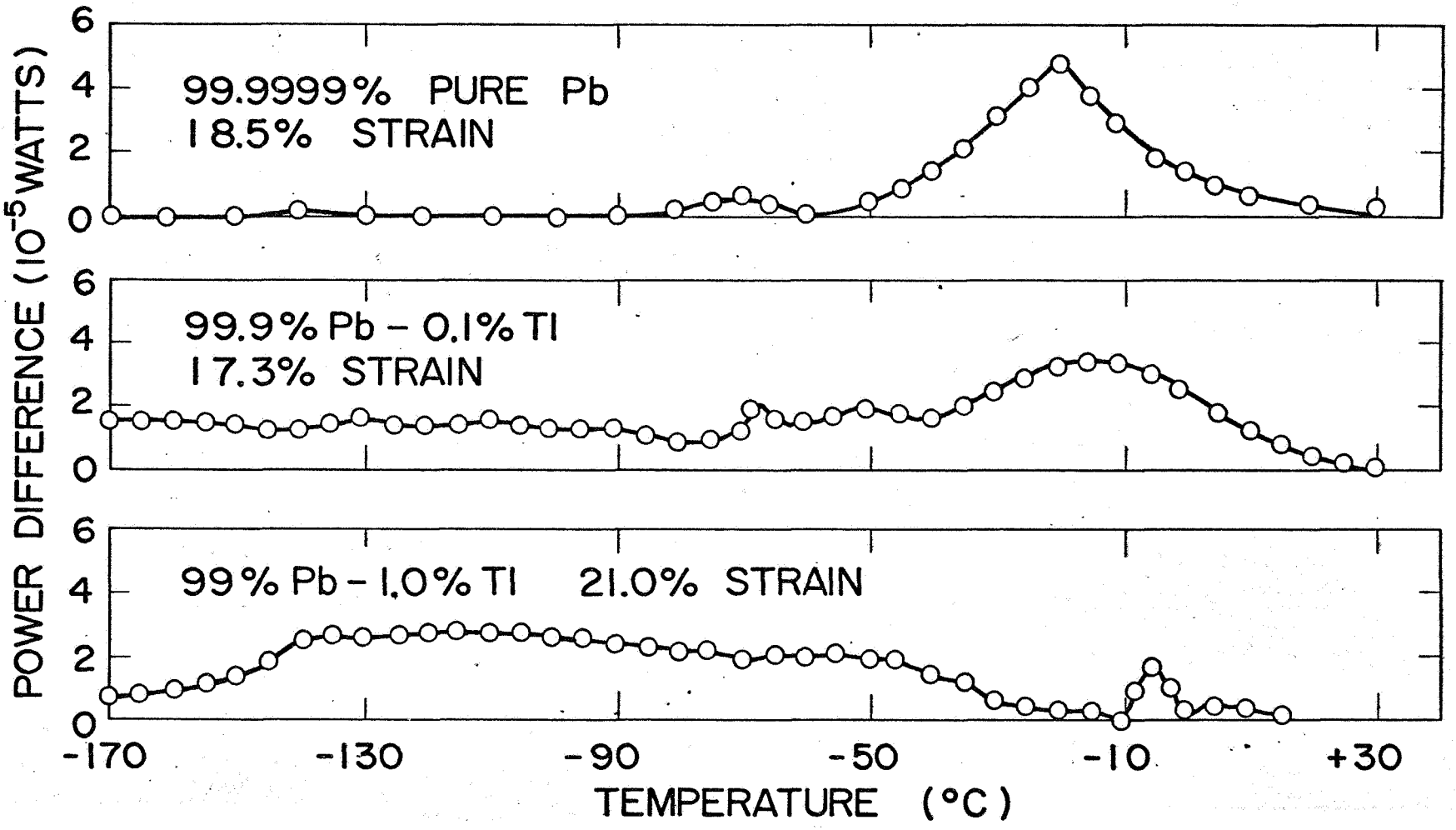
99.9999% PURE Pb
18.5% STRAIN
99.9% Pb – 0.1% Tl
17.3% STRAIN
99% Pb – 1.0% Tl 21.0% STRAIN
POWER DIFFERENCE (10^{-5} WATTS)
0
2
4
6
-170
-130
-90
-50
-10
+30
TEMPERATURE (°C)

Figure 3

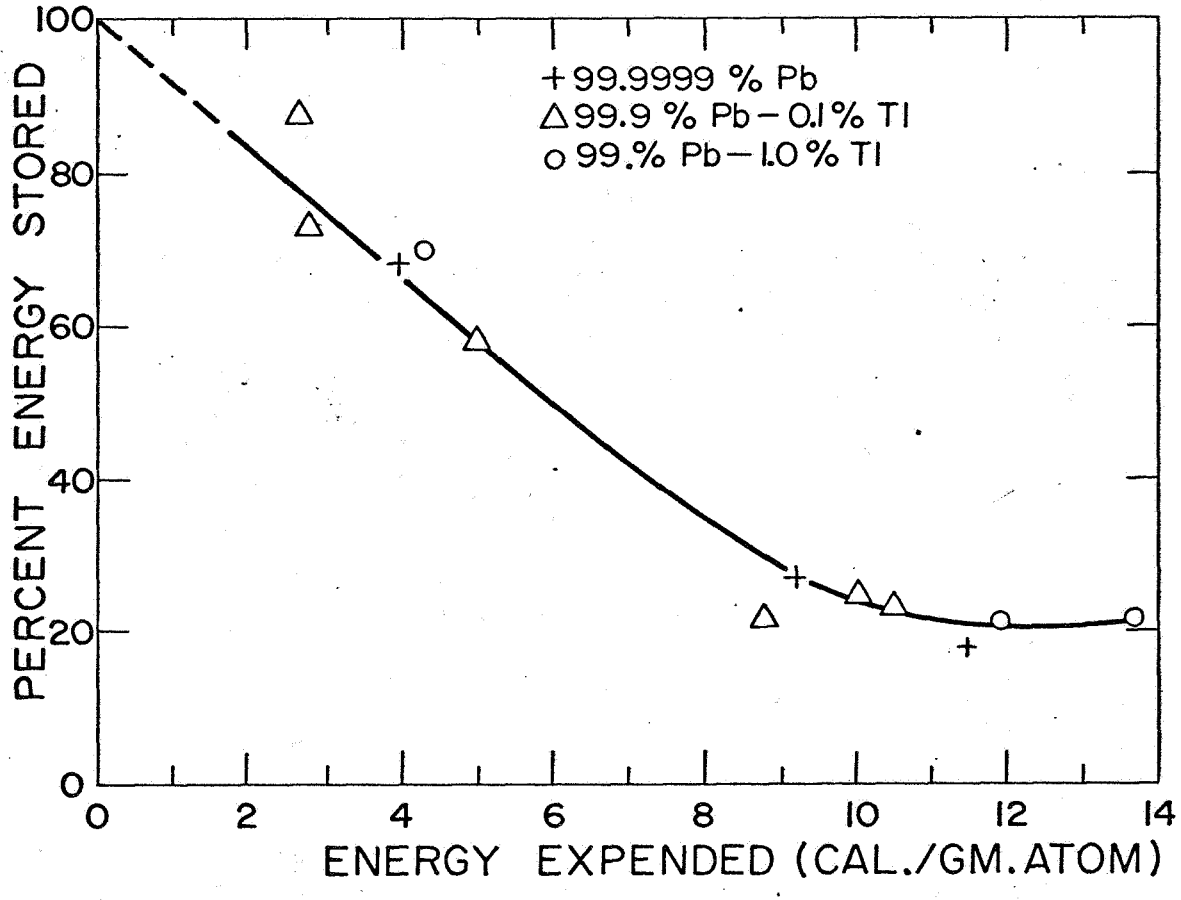
100
80
60
40
20
0
PERCENT ENERGY STORED
+ 99.9999 % Pb
△ 99.9 % Pb – 0.1 % Tl
○ 99.% Pb – 1.0 % Tl
0
2
4
6
8
10
12
14
ENERGY EXPENDED (CAL./GM. ATOM)

Figure 4

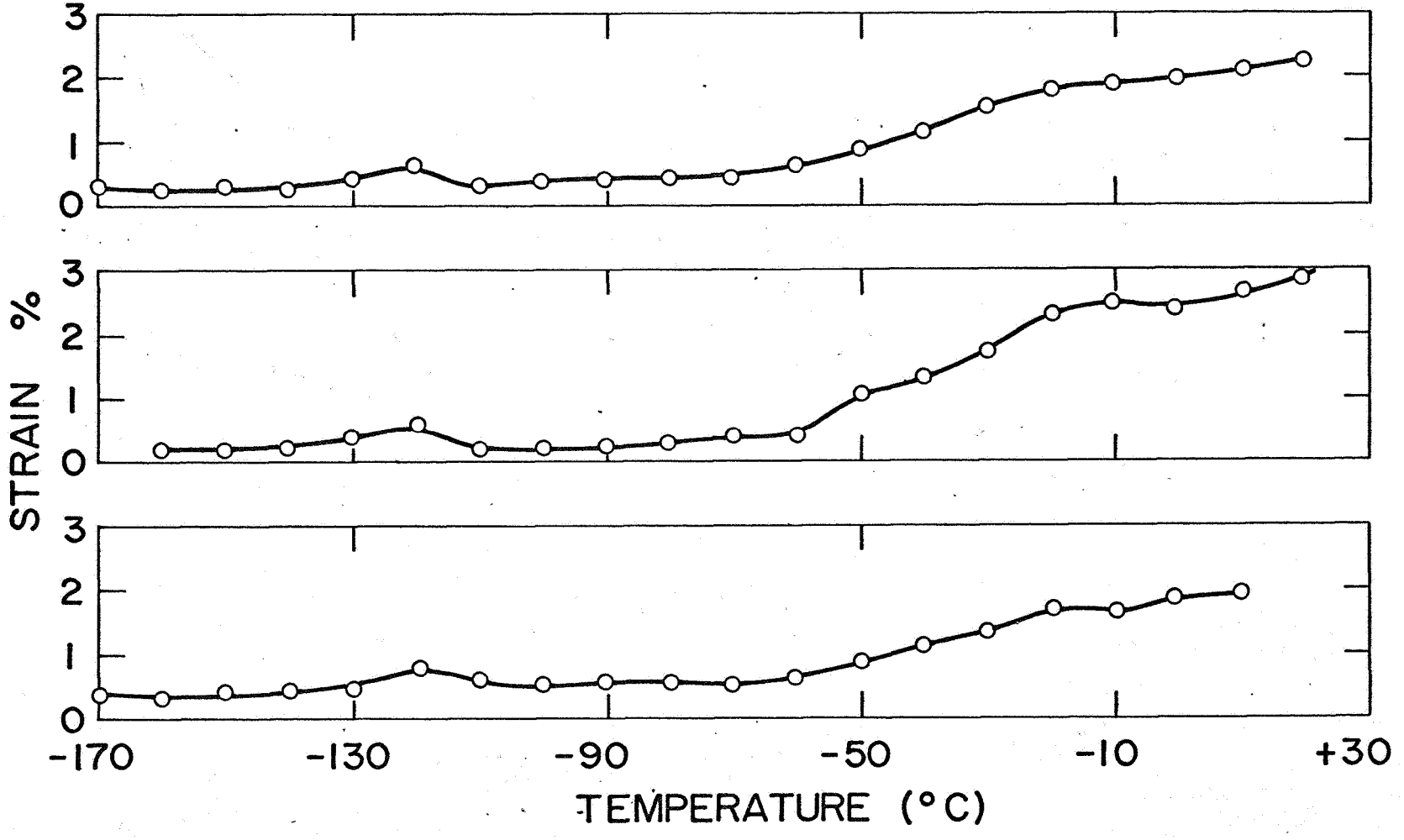

Figure 5

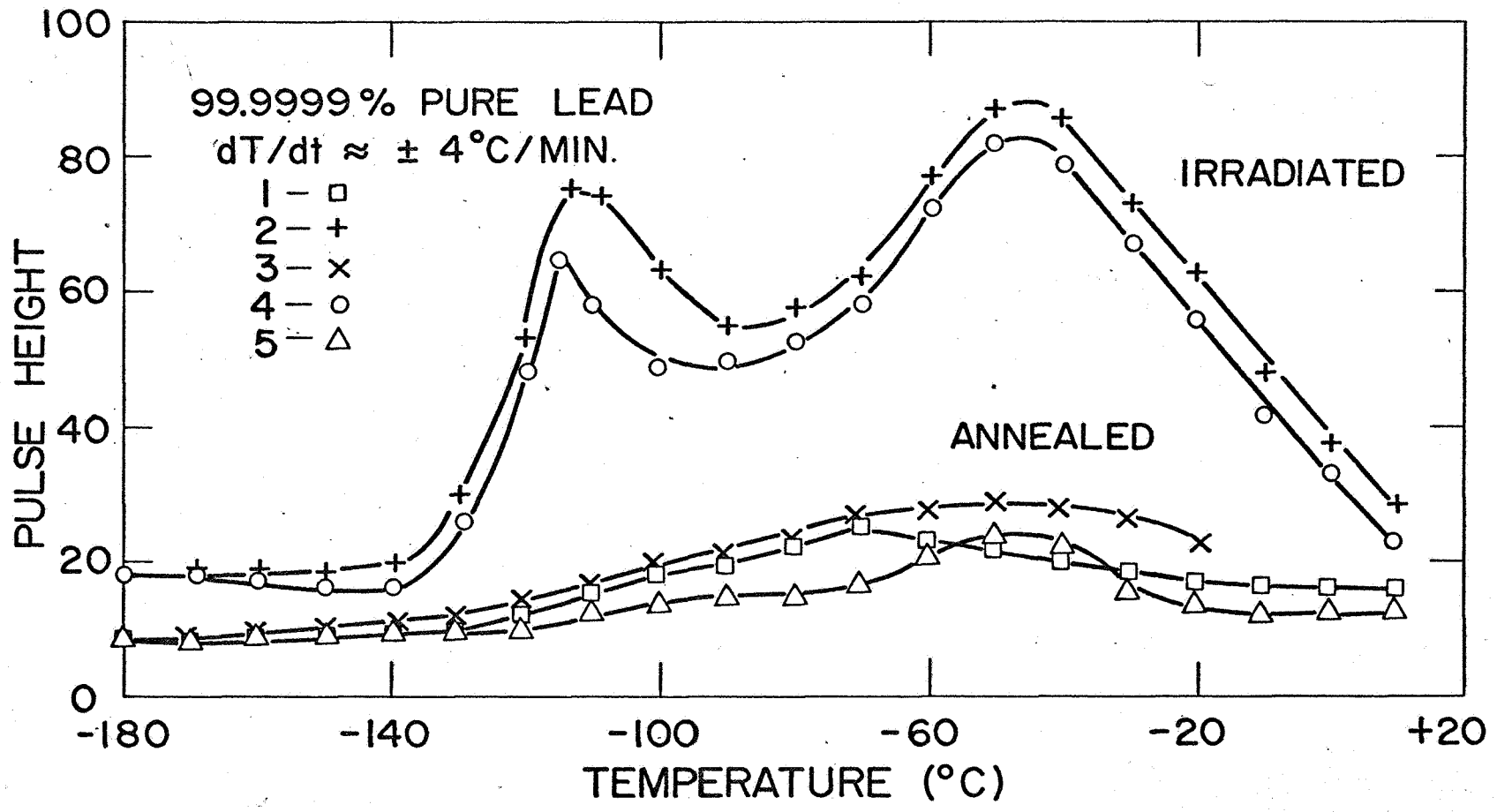
99.9999% PURE LEAD
dT/dt ≈ ± 4°C/MIN.
1 — □
2 — +
3 — ×
4 — ○
5 — △
IRRADIATED
ANNEALED
PULSE HEIGHT
TEMPERATURE (°C)
100
80
60
40
20
0
-180
-140
-100
-60
-20
+20

Figure 6

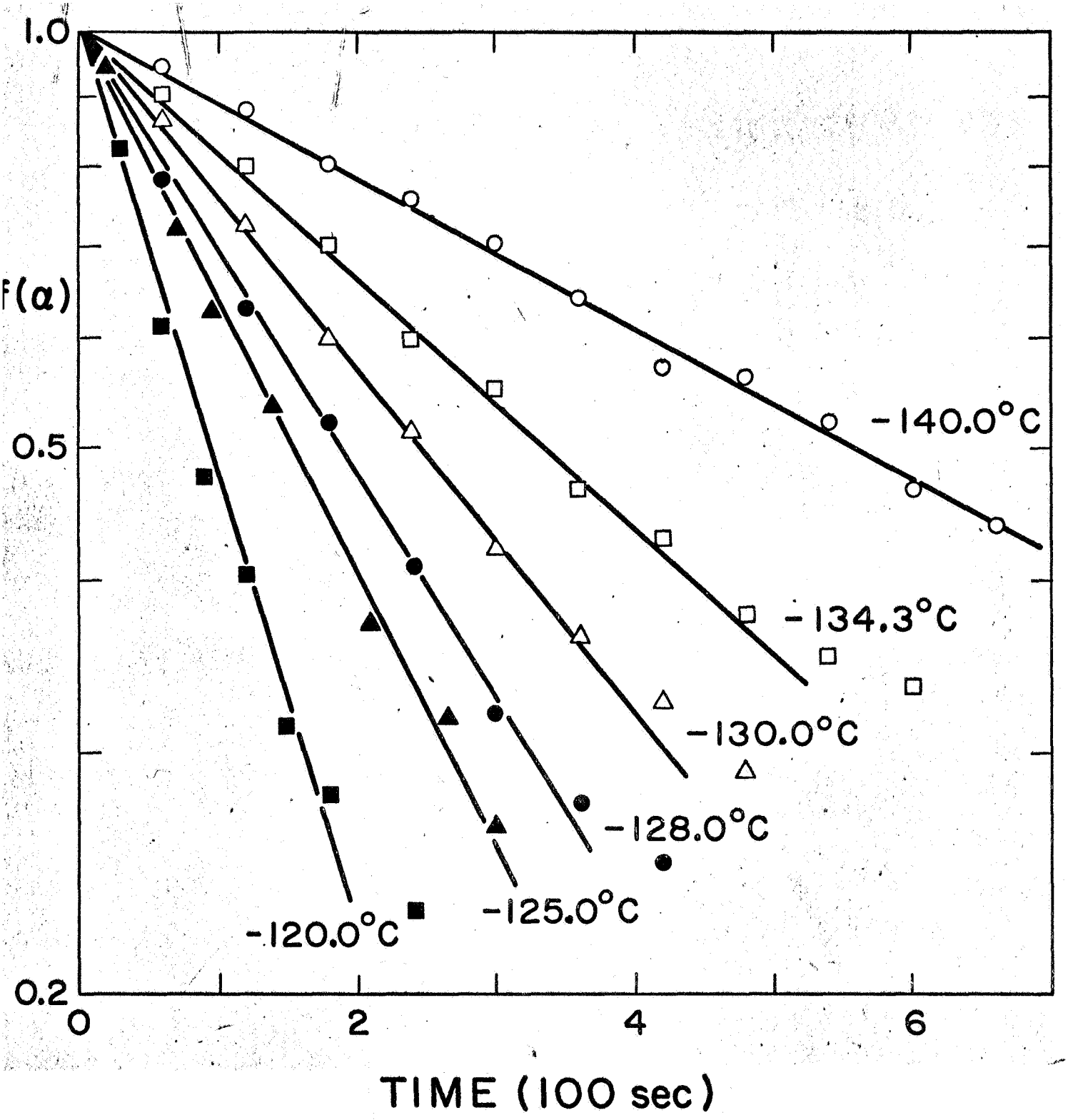
1.0
0.5
0.2
F(α)
0
2
4
6
TIME (100 sec)
-140.0°C
-134.3°C
-130.0°C
-128.0°C
-125.0°C
-120.0°C

Figure 7

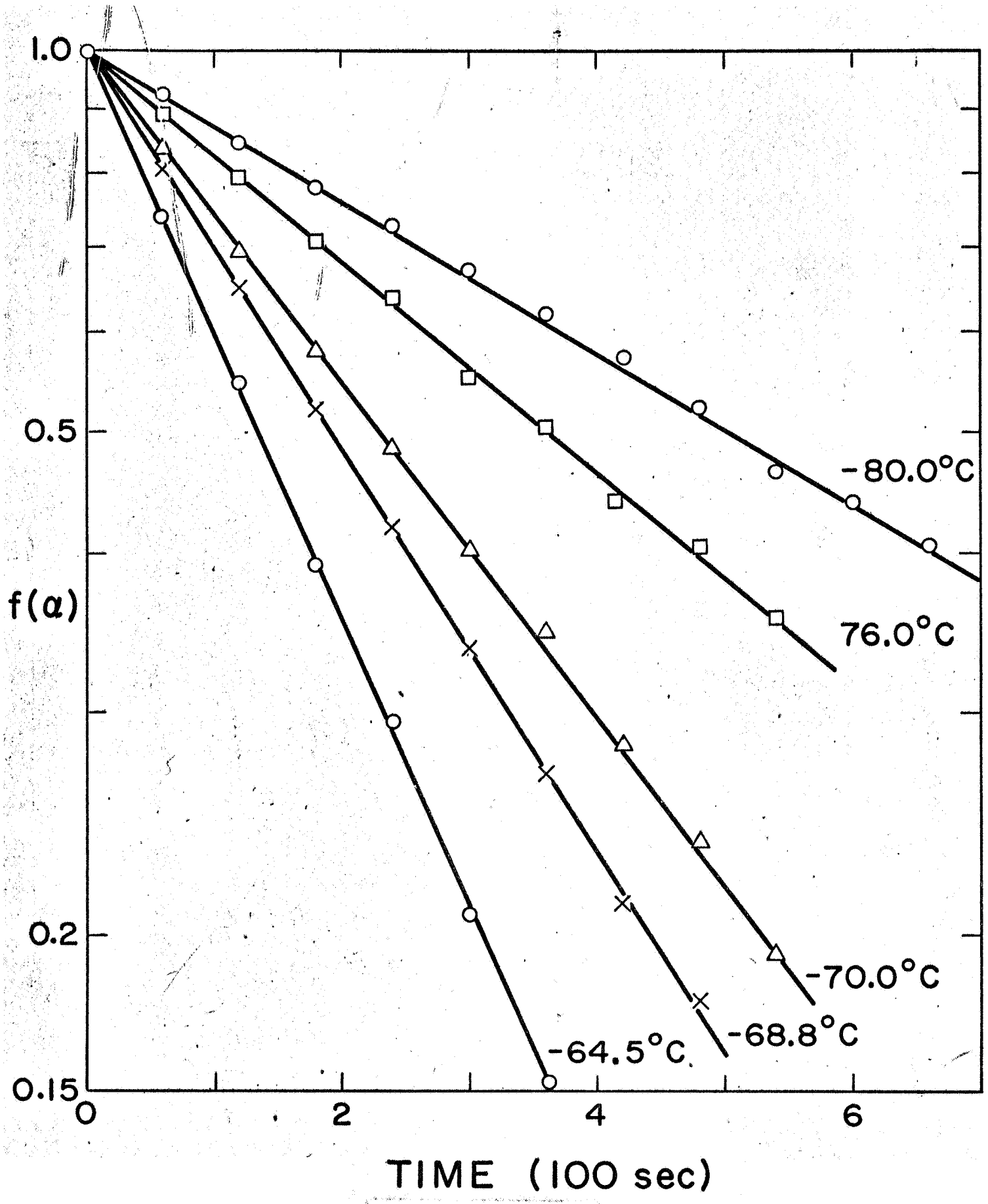

Figure 8

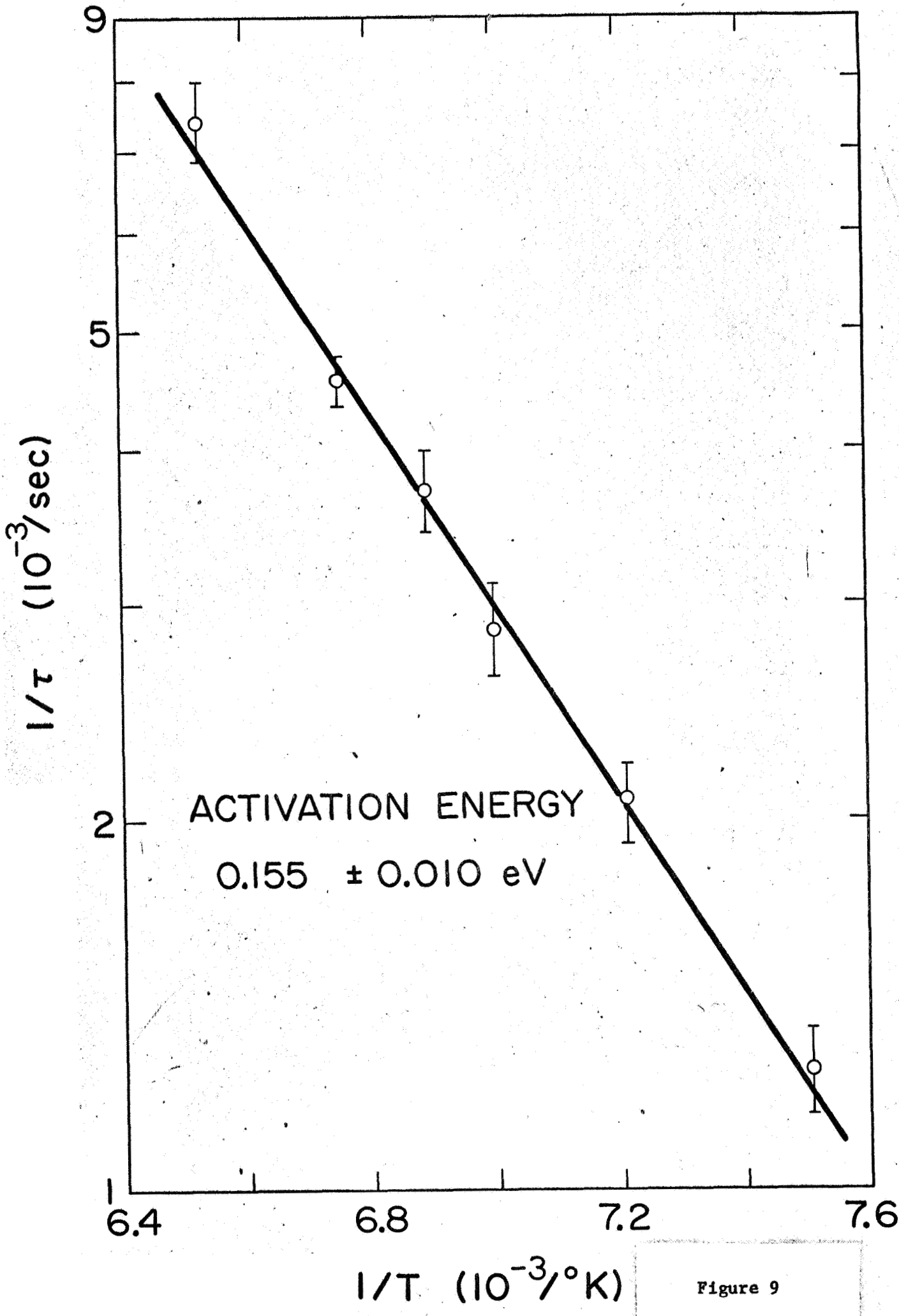
9
5
2
1
1/τ (10⁻³/sec)
ACTIVATION ENERGY
0.155 ± 0.010 eV
6.4
6.8
7.2
7.6
1/T (10⁻³/°K)

Figure 9

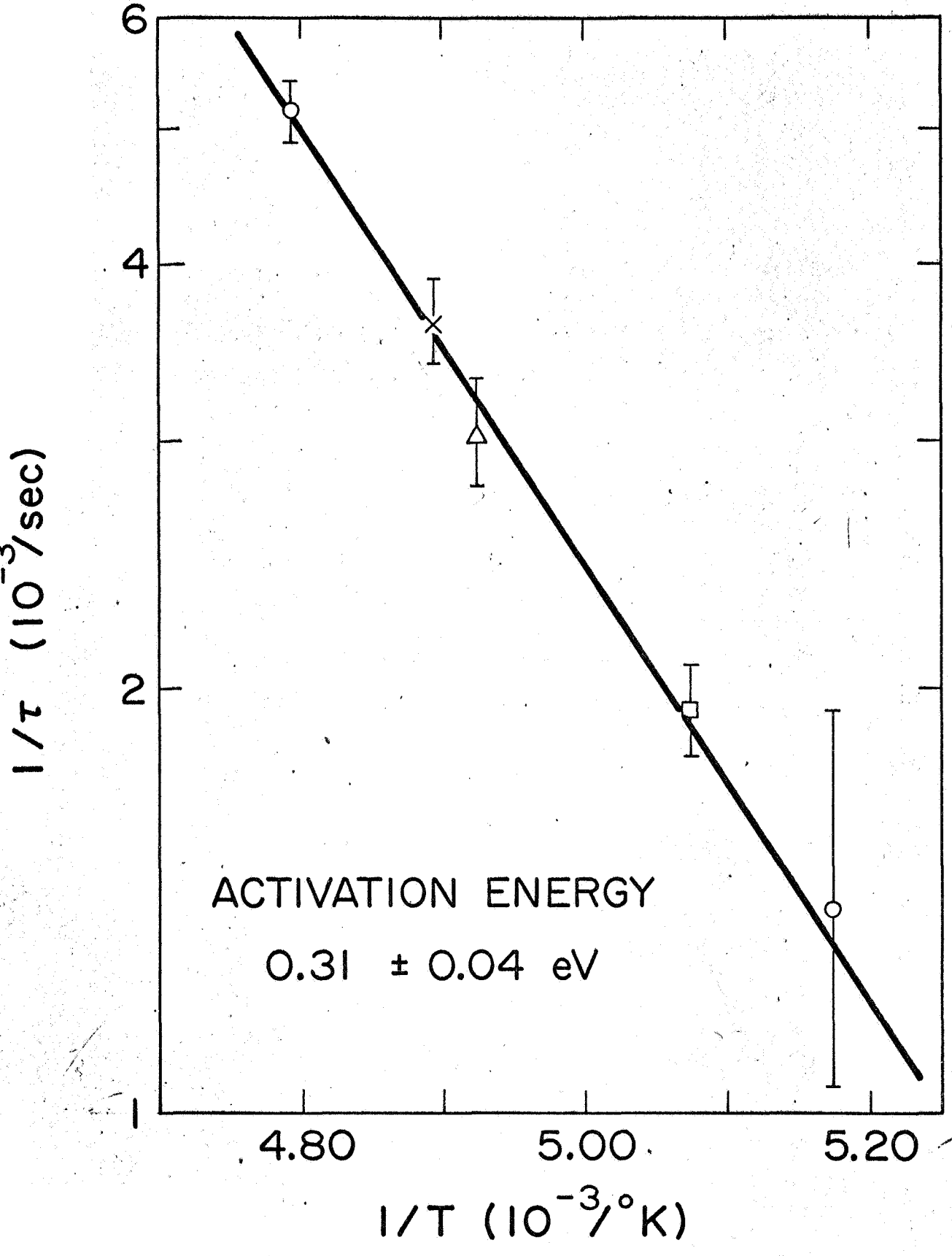
6
4
2
1
1/τ (10⁻³/sec)
ACTIVATION ENERGY
0.31 ± 0.04 eV
4.80
5.00
5.20
1/T (10⁻³/°K)

Figure 10